

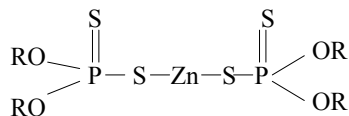
# PREPARATIVE ISOLATION AND CHARACTERIZATION OF ZINC DIALKYL-DITHIOPHOSPHATES FROM COMMERCIAL ANTIWEAR ADDITIVES

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## Introduction

Improvement of lubricant oil performance is achieved by additivation with tailor-designed products for specific purposes<sup>1,2</sup>. Zinc Dialkyl-Dithiophosphates (ZnDTP) exert antiwear actions over diverse components from internal combustion engines. Their synthesis comprises the generation of dithiophosphoric acid from  $P_2S_5$ , reaction of the acid with one alcohol and then with ZnO. Their structural formula is:



The efficiency, thermal stability and cost of ZnDTP's depend on the chosen alcohol<sup>2</sup>. Derivatives can be easily identified by typical vibrational frequencies for the P-O-C bond in the infrared spectrum (IR)<sup>3</sup>. P-O-C moieties with R groups from primary alcohols display bands at  $1000\text{ cm}^{-1}$ , from secondary at  $980\text{ cm}^{-1}$  and aryls at  $920\text{ cm}^{-1}$ .

Preparative isolation of ZnDTP's has been reported by dialysis<sup>4</sup>, thin layer chromatography<sup>4,6-7</sup>, open column liquid chromatography<sup>3,5,8</sup>, high performance liquid chromatography (HPLC)<sup>3,4,9-10</sup> and gel permeation chromatography<sup>11</sup>. Supercritical fluid chromatography has been reported for analytical scale separation<sup>12</sup>.

Spectrometric techniques are useful for determination of the distribution of ZnDTP mixtures. Mass spectrometry allows determining the alkyl length of the R substituents<sup>13</sup>. ZnDTP direct separation and characterization has been reported by coupled liquid chromatography-mass spectrometry<sup>14</sup> and by selective ionization mass spectrometry without prior separation<sup>15</sup>. Nuclear magnetic resonance spectrometry has proven useful for elucidating ZnDTP intermolecular complexation and interaction between solvents and these organometallic compounds as well<sup>16</sup>.

Chemical derivatization and analysis of reaction products is another strategy followed for the characterization of ZnDTP. Lithium Aluminum Hydride gives origin to the original alcohols used during the synthesis of ZnDTP<sup>17</sup>. Alkyl-iodides are generated by the action of HI<sup>18</sup>. Dialkyl-methylthiophosphates are the products derived from the action of  $\text{CH}_3\text{I}$ <sup>19</sup>.

The objective of this work was to develop a fast, preparative and automated methodology for isolation of ZnDTP compounds from commercial additive packages. This was achieved by HPLC, allowing to quantify the total amount of these antiwear components in each received production batch. Further, isolated ZnDTP concentrates were characterized by IR and reverse phase HPLC for qualitative monitoring commercial ZnDTP batches employed for the formulation of end lubricant products.

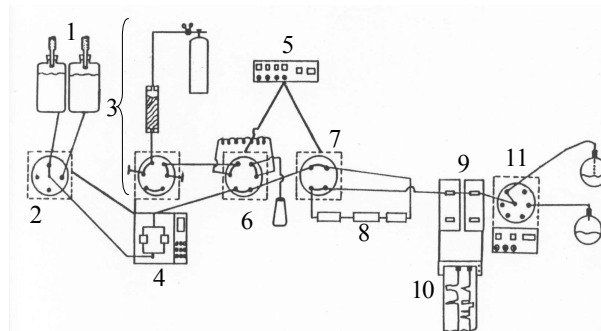
## Experimental

**HPLC system and operating conditions for the preparative isolation of ZnDTP from commercial additives.** The HPLC schematic is presented on Figure 1. A Waters 590 EF programmable pump delivers solvents and controls two pneumatic actuated valves, viz, a solvent select valve and a six-port switching valve used for

sample solution delivery. Sample solution was placed inside an Altex gas-tight glass column connected to a pressurized (5 psig) nitrogen source used for pushing the solution into the sampling loop. Typically, 500 mg were injected on each separation. A DVSP-4 digital valve sequence programmer from Valco commands the actuation of two pneumatic valves, viz, a Rheodyne 7010 injection valve provided with a 1 mL loop and a 4-port backflush N6 valve from Valco. A Glenco 5480 Uv-Vis detector set at 254 nm and a Knauer 98:00 RI detector were used for elution monitoring. Detector signals were registered with a Linear chart recorder. Separated fractions were collected with a Glenco 410 programmable fraction collector, provided with a 6+1 port Rheodyne 7060 distribution valve.

A bank of three silica columns connected in series was used to carry out the separations. The columns were slurry packed at 12000 psi with the aid of a Haskell air driven pump. Adsorbosil LC (10  $\mu\text{m}$ , irregular) from Alltech was used as packing material. Adsorbent drying prior to packing was achieved inside an oven kept at  $100^\circ\text{C}$  (24h). Column dimensions were 25cm x 1cm.

Base oils (excipient) were eluted during 30 min with a mixture n-C6/CCl4: 75/25: vol. in forward flow set at 5 mL/min. ZnDTP components were recovered under backflush (B.F) with  $\text{CHCl}_3$  at 14 mL/min, during a 10 min period. Column regeneration with the initial solvent mixture was achieved by delivering the solvent at 16 mL/min during a period of 10 min. The whole separation was achieved in 50 minutes. Pooling of fractions separated during successive separations was possible. The 590 EF Waters pump was used to generate the pulses commanding the whole automated separation and collection sequence brought by the valve actuator/fraction collector.



**Figure 1.** Preparative HPLC Schematic. 1: Eluents. 2: Solvent proportioning valve. 3: Sample delivery device. 4: Solvent pump. 5: Programmable valve controller. 6: Injection valve. 7: Backflush valve. 8: Column bank. 9: HPLC detectors. 10: Chart recorder. 11: Fraction collector.

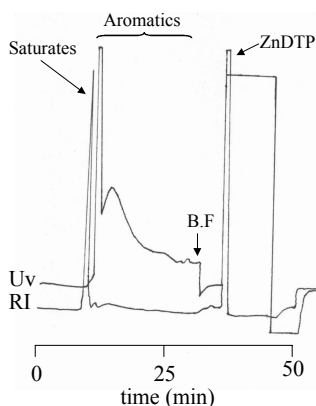
**Infrared spectrophotometry.** IR spectra were acquired on a Pye-Unicam SP 1100 spectrometer in the range from 4000 to  $400\text{ cm}^{-1}$ . Small amounts of neat separated base oils or isolated ZnDTP concentrates were compressed between a couple of KBr windows.

**Reversed phase HPLC of ZnDTP concentrates.** Isolated ZnDTP concentrates were dissolved in  $\text{CH}_2\text{Cl}_2$  and injected in a stainless steel column (slurry packed at 12000 psig with the aid of a Haskell pneumatic pump). Spherical octadecyl derivatized silica (RPC18) of 5  $\mu\text{m}$  from E-Merck was the column adsorbent. The silica was further end-capped by reaction with trimethylchlorosilane. Sample injection was performed with a Rheodyne 7410 valve provided with an internal built loop of 1  $\mu\text{L}$ . Elution with  $\text{CH}_3\text{CN}$  at 250  $\mu\text{L}/\text{min}$  was carried out with a Waters 590EF pump. Uv detection at 240 nm was achieved with an LDC Spectromonitor II

HPLC detector. Chromatographic signals were digitalized with an A/D converter and feed to an HP-1000 computer provided with a LAS (laboratory automation system).

## Results and Discussion

Chromatographic conditions for the preparative separation and isolation of excipient (base oil) from active compounds (ZnDTP) present in commercial antiwear additives, were found during this study. Separations can be run in a reasonable time span (50 min). However, the most important advantage of the developed methodology lies on the fact that columns are reusable, aspect verified with one column bank used during a 1 month period for ca. 100 sample injections. A typical separation is presented on **Figure 2**. The preparative isolation gave the total amount of ZnDTP contained in each commercial batch of additive. This value is an important input for quality assurance for the end lubricant products. Further, the availability of mg-g quantities of the active compounds, allowed to characterize these materials in greater detail. Also, the physical availability of grams of these materials permitted their use in pilot studies conducted with combustion motors.



**Figure 2.** Typical chromatogram for the preparative separation of the active ZnDTP components from a commercial antiwear additive.

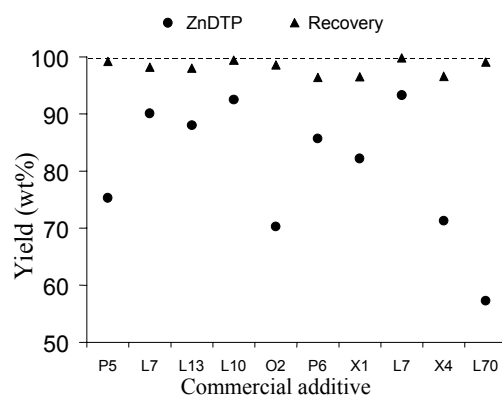
The repeatability of the preparative separations can be estimated by triplicate results for one sample, presented on **Table 1**. It was deemed reasonable for the aimed purposes of the study. The yields of ZnDTP components for some commercial additives can be appreciated on **Figure 3**. On the same figure, fraction recoveries are included. Recoveries were deemed good, averaging  $98.4 \pm 1.4$  wt%.

**Table 1. Repeatability for the HPLC Separation of a Commercial ZnDTP Additive (P5).**

Run	% wt Oil	% wt ZnDTP	Recovery (%wt)
1	21.9	75.3	99.2
2	23.7	74.7	98.4
3	23.4	77.2	100.6

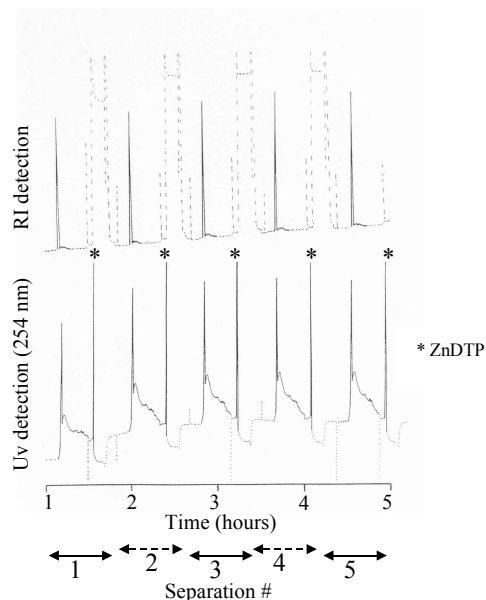
Separation of gram amounts of ZnDTP required the automated operation of the HPLC system. This commonly was carried out during overnight runs that allowed collecting ca. 5g of active materials in 12 separation cycles. **Figure 4** presents the initial portion for a typical chromatographic display of an automated separation sequence.

Characterization of ZnDTP mixtures can be practiced following different approaches, as cited in the introduction. With the preparatively isolated materials obtained in this work, qualitative



**Figure 3.** Yield of ZnDTP for commercial antiwear additives and recovery of separated fractions during the preparative HPLC isolation.

characterization was performed both by IR and reverse phase HPLC. On **Figure 5**, IR spectra of one oil fraction and three active (ZnDTP) fractions are presented. Absence of ZnDTP characteristic signals near  $1000\text{ cm}^{-1}$  can be evidenced for the oil fraction, guarantee an efficient separation. IR spectra in the frequencies comprised between  $1600\text{--}600\text{ cm}^{-1}$  can be considered as fingerprints for each ZnDTP mixture. The examples included in **Figure 5** illustrate this aspect. Partial contribution of primary/secondary alkyl or aryl alcoholic R substituents can be deduced from the spectra, according to the literature assignments<sup>3</sup> for the P-O-C band near  $1000\text{ cm}^{-1}$ .



**Figure 4.** Chromatograms for a typical automated HPLC separation sequence of a commercial ZnDTP additive.

Reverse phase HPLC fingerprintings of ZnDTP active mixtures isolated from commercial additives are illustrated with the examples presented on **Figure 6**. The technique allows differentiating among diverse commercial ZnDTP. Also, subtle differences in mixture distributions can be detected among diverse batches of the same product, as evidenced with the example included in the same figure.

As a final remark it is to be said that the HPLC preparative separation methodology has been successfully applied for the isolation of the medium polarity components included in multipurpose additive mixtures used in lubricant products. It fails for high polarity compounds like sulphonates, which remain irreversibly adsorbed over the packing material. Recently, environmental constraints made  $\text{CCl}_4$  disappear from the market. We have substituted it by MTBE (Methyltertbutylether). Equivalent polarity mixtures have been prepared following the procedures described by Snyder and Kirkland<sup>20</sup>. With the n-C6/MTBE eluent, successful separations of end product lubricants have been carried out for exci-

ipient isolation. However, no attempts have been made to recover the additives in these cases since base oils were the targeted analytes.

## Conclusions

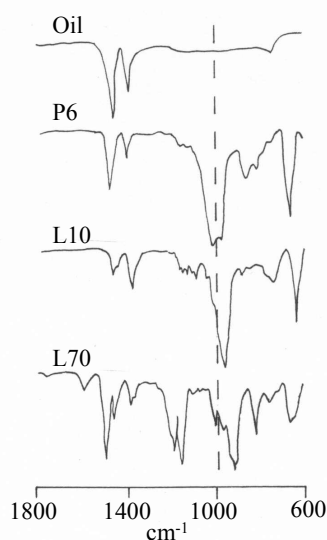
A preparative and automated HPLC separation methodology was developed for isolation of ZnDTP components from commercial antiwear additives. The methodology relies on rugged silica columns, which can be reused for long periods of time (months). Preliminary estimations suggest that separation repeatability and fraction recoveries were good.

Qualitative characterization of isolated ZnDTP mixtures was easily achieved by IR spectrophotometry and by HPLC. IR can assess the gross nature of ZnDTP alcoholic moieties. Fingerprints of diverse commercial mixtures and even subtle differences among diverse batches of the same product are obtained by reverse phase HPLC.

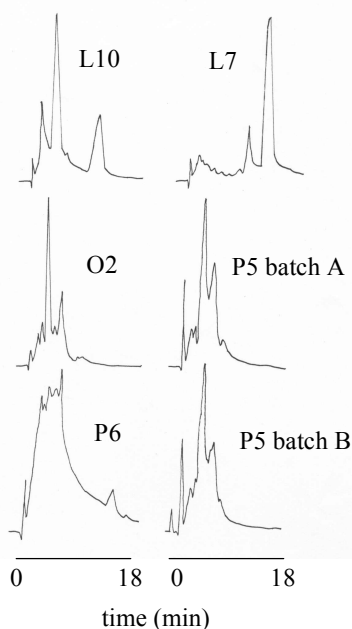
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**Figure 5.** Infrared spectra for one separated oil fraction and for three active ZnDTP isolated active components.



**Figure 6.** Reverse phase HPLC fingerprinting of isolated ZnDTP active components from commercial antiwear additives.